

FILM DEPOSITION AND CONSOLIDATION DURING THIN GLOVE COAGULANT DIPPING

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ABSTRACT

In this paper we examine the rate of film build-up and the evolution of polymer volume fraction in coagulant dipped films. The results are for nitrile and natural rubber compounds.

We describe a model for the build-up of a latex film that coagulates onto a former as a wet gel and consolidates by a wet sintering process. We achieve this by applying diffusion and reaction kinetics for the coagulant transporting from a former into the latex bath. Wet sintering, the underlying mechanism for serum exudation from the wet gel, is modelled for a consolidating aggregate of latex particles. The parameters used in the models are either measured in separate experiments or are available from the literature.

We compare the model predictions with the experimental results. The first, rapid, stage of film build-up is modelled successfully by simple diffusion of the coagulant cations. At longer dwell times, it is found that the reaction between coagulant and surfactant is the primary mechanism for the rate reduction.

The rate of consolidation of the wet gel could be modelled reasonably well using a previously developed equation for latex film formation. The rate was chiefly dependent on the stress relaxation modulus of the polymer.

KEYWORDS: Glove Dipping, film formation, diffusion, colloid stability, sintering

INTRODUCTION

Industrial relevance of the current work

Thin elastomeric gloves are currently the most important products made by the coagulant dipping process, finding use in the medical, scientific, food and many other areas. Their production has become a significant industry, with an estimated value of just over US\$5 billion in 2014.¹ However, much of the technology that is employed in their manufacture is empirical, gained through trial and error in laboratories and, more frequently, on production plants.

The primary purpose of almost all dipped products is to act as a barrier, often to bacteria, viruses, fluids or chemicals that present hazards to health. At the heart of the dipping process is the formation of a film of the elastomer, the film that is the protective barrier during the glove's use. It is therefore clear that a good, representative theoretical model of film formation during the dipping process would greatly assist and accelerate technical progress in improving the performance of dipped products.

Description of the coagulant dipping process

A schematic diagram of the main steps in the coagulant dipping process is shown in Figure 1. A suitable mould or former, often made of unglazed ceramic, is firstly coated with a very thin layer of coagulant solution, commonly calcium nitrate in water. To achieve the thin coating, the former is dipped into and withdrawn from the coagulant solution. On withdrawal, the former enters an oven so that the coagulant solution is partially or completely dried. Calcium nitrate is hygroscopic, so in normal dipping conditions, even if it is dried completely, it rapidly absorbs atmospheric moisture. The coagulant layer on the former at the next stage

of the process is therefore likely to be in the form of a concentrated solution.

The compound used for coagulant dipping is aqueous latex mixed with relatively small amounts of pigments and vulcanisation chemicals. The compound is diluted and pH adjusted as considered necessary.

The coated former is dipped into the compound to the required depth. The high coagulant concentration at the former's surface causes the colloidal particles adjacent to the former to flocculate, creating a spongy solid film, often termed the "wet gel". The thickness of the wet gel is found to increase as the time of immersion in the compound (the dwell time) increases. After the desired dwell time, normally determined by trial and error to give the required final film thickness, the former is withdrawn from the compound. The assembly is then moved into an oven where the wet gel is dried.

Optionally, before the film is fully dry, the former can be removed from the oven and immersed in water for perhaps 30 to 60 seconds. This process, known as leaching, removes some of the water-soluble non-rubber materials from the elastomer. After leaching, the assembly is returned to the oven to complete the film drying. Finally, the dry film is removed from the former to yield the elastomeric product.

Industrial experience is that varying the concentration of the latex dispersion, the dwell time in the latex dispersion and the concentration of the coagulant solution can control the thickness of the final film.

General description of latex film formation

The process of film formation, through the evaporation of water from polymer dispersions, has been studied extensively over the past 60

years.^{2,3} The transformation of a colloidal dispersion into a continuous, mechanically robust polymer film is generally thought to occur via three steps. Initially, evaporation brings the particles into contact, in some form of close packing. The particles then begin to sinter and consolidate, increasing the local volume fraction. Depending on the process temperature and polymer glass transition temperature (T_g), there are three possible driving forces for particle deformation at this stage. At high drying temperatures with respect to its T_g , the polymer's viscosity & modulus are low and the particles deform because of the action of the polymer-water interfacial tension. This is called wet sintering and the deformation occurs more rapidly than evaporation.^{4, 5} As the relative drying temperature is decreased, the polymer modulus is increased (sharply so in the T_g region), deformation and wet sintering are slower and evaporation of the liquid phase leads to menisci forming at the air-liquid interface, causing a negative capillary pressure to develop in the remaining liquid. This decrease in pressure can be thought of as a compression because of atmospheric pressure acting on the top surface of the film. The magnitude of the capillary pressure scales with the inverse of the particle size and can reach many MPa. This mechanism is called capillary deformation and occurs concurrently with evaporation.^{3,6,7} At even lower drying temperatures compared to T_g , the polymer modulus becomes very high and there may be little deformation upon complete evaporation of the liquid phase. In this case, there remains the driving force of polymer - air interfacial tension that can cause further coalescence. This process, known as dry sintering⁸ is likely to be slow.

A model that describes the different driving forces and determines the temperatures over which each of the different sintering

mechanisms are observed, has been described by Routh and Russel.^{9,10}

The film formation process involved in coagulant dipping is slightly different to that of evaporative drying described above. Exposing the relatively dilute polymer dispersion, very rapidly, to coagulant results in an expanded three-dimensional network of touching particles, with a similar polymer concentration to that of the host dispersion.¹¹ As the particles are brought into contact and before any liquid evaporation has taken place, the wet sintering mechanism will begin to operate. The polymers used in glove dipping are invariably of low modulus, so deform relatively rapidly due to the polymer-liquid interfacial tension. Wet sintering causes the three-dimensional network to contract as each individual particle - particle interface starts to coalesce. Experimental work reported earlier¹¹ suggests that the rate of shrinkage due to wet sintering is slow with respect to the coagulative film growth.

On withdrawal of the former from the latex, it is often observed that clear serum is expelled from the wet gel. This is almost certainly a result of the wet sintering shrinkage. The term syneresis is often used to describe this phenomenon.

Normally, shortly after the former is withdrawn, it enters a drying oven where particle coalescence and liquid loss continues. The oven causes the rate of evaporation to increase. Additionally, the increased temperature will reduce the polymer modulus and consequently increase the rate of wet sintering shrinkage. Once sufficient water has evaporated to give liquid menisci in the film surface, film formation continues as described by the normal evaporative model.

The dipping process - available published work

Despite the reported ~180 *billion* rubber gloves now produced each year,¹ very few studies of

the physical and chemical processes involved in coagulant dipping have been published in the open literature.¹²⁻¹⁶

Gorton's papers^{12, 13} report film build-up for a variety of natural rubber compounds, as a function of compound viscosity and dwell time. Coagulant dipping was done on top of a thin, dried, straight (non-coagulant) dip of the compound. Cyclohexylamine acetate was used as coagulant in most of the experiments and the compound total solids content (TSC) was in the range of 50 to 65 wt%. The film thickness was measured directly on dried film samples. Gorton found that the build-up of film thickness was linearly dependent on the square root of dwell time and on \log_{10} compound viscosity. The square root dependency supports the common assumption that film build-up is controlled, at least in part, by the diffusion of coagulant.

Examination of Gorton's data indicates that there was an initial rapid rate of dry film build-up that decreased as dwell time increased, giving a departure from the $t^{1/2}$ dependence. The departure was more apparent with the lower (50 wt%) TSC compounds and was evident with and without applying a correction for the thickness of the straight dip.

The paper of Stewart¹⁴ contained a theoretical treatment of the coagulant dipping process for poly(chloroprene) latex, but the assumptions made and experimental conditions used are now worth re-visiting in the light of developments, both theoretical and practical, since its publication over 40 years ago. The theory and most of the results presented by Stewart were concerned with latex at high solids content (65 wt%), which was assumed to produce a coagulated wet gel with a polymer volume fraction of 74 %.

Stewart's experimental procedure was somewhat unusual in having the latex contained in a vertical glass tube, the bottom of which was

covered with an open mesh net pre-treated with coagulant. The tube was immersed in a bath of coagulant solution for the desired time, after which the coagulated film was removed from the tube and its thickness measured with a gauge. Stewart assumed that coagulative growth was caused by the diffusion of Ca^{2+} ions, and hence governed by the diffusion equation. He used a model for the wet sintering of two spheres to calculate the time dependence of the volume fraction of fluid in the wet gel. It was assumed that there was no gradient in fluid volume fraction across the film thickness. The decrease in fluid volume fraction was used to correct the diffusion rate. The precipitation of surfactant by calcium ions was acknowledged, in that it was used as the criterion for coagulation and as a possible reason for the inhibition, in some cases, of coalescence of latex particles. Stewart observed that as the latex modulus decreased, the build-up rate decreased. This was attributed to faster coalescence reducing the cross sectional area through which the calcium ions can diffuse.

The paper of Blackley *et al.*¹⁵ described a thorough quantitative examination of key variables in the coagulant dipping process, including solids content and surfactant concentration, but did not consider the detailed theory and mechanisms of the process. Their study was confined to natural rubber latex at concentrations of 20 to 60 wt%, with most of the results obtained at 50 wt%. They showed the thickness of the film increasing with dwell time and discussed how a $(\text{time})^{1/2}$ relationship was consistent with a diffusional process. For one series of experiments, Blackley calculated the wet deposit thickness (from the measured dry thickness values) and presented them as a function of $(\text{dwell time})^{1/2}$. He found a faster film build-up as the mix solids was reduced, which was attributed to a diffusion path for the calcium

ions becoming less tortuous. Blackley also presented these build-up rate results as having two linear regions, with a greater slope at lower (< 5 min) dwell times. However, some additional results were shown that caused the authors to conclude that this apparent two-stage process was perhaps an artefact of the experimental procedure.

Sasidharan *et al.*¹⁶ also studied various practical aspects of dipping high solids (50 wt%) natural rubber compounds, including film build-up rate. The film thickness after drying was measured directly. Generally they found a sharp increase in thickness up to 50 seconds dwell time, but only a marginal increase thereafter. The rate reduction was attributed to the immediate formation of a layer of rubber coagulum, through which coagulant ions had to diffuse.

The Present Work

The studies mentioned above, concentrated on high solids polymer dispersions. The model and experimental work presented here considers the colloidal coagulation of more dilute polymer dispersions that are necessary to create the thin (< 0.1 mm) gloves produced today. At low solids content, there may be significant differences in compound viscosity and coagulant diffusion, compared with the high solids case. Both these factors are of interest in the dipping process. The polymers used in this study are nitrile latex and natural rubber, which are the dominant materials currently used to make thin gloves. Probably the most important stage in the dipping process is the build-up of polymer on the former. We build upon the previous studies, mentioned above, to generate a first principles model for the growth of the wet gel. In addition, the present work provides a model for wet sintering/syneresis. We achieve this by applying diffusion and reaction kinetics to the coagulant transporting into the latex bath. A range of

models based on these physical processes are explored.

The wet sintering is modelled by applying the Routh and Russel model^{9, 10} to a growing aggregate of latex particles. We discuss how the film thickness and average volume fraction can be affected by the different experimental parameters. Finally, we compare the experimental and numerical results.

EXPERIMENTAL

Materials

Latexes

Two latexes were used in this study:

- 1) A laboratory synthesized, standard carboxylated nitrile latex (XNBR) of the type that is used commercially in the production of dipped gloves. XNBR is a copolymer of butadiene, acrylonitrile and methacrylic acid. The latex used here contained about 30% by weight of acrylonitrile and about 5% of methacrylic acid.
- 2) Unvulcanised natural rubber (NR), obtained from Synthomer Sdn Bhd, Malaysia.

Zinc Oxide

ZnO was obtained as a 50% dispersion from Aquaspersions Ltd, Halifax, UK.

Methods

Particle Size

The average latex particle size was measured by dynamic light scattering, using a Brookhaven ZetaPALS.

Interfacial Tension

The interfacial tension between the polymer and aqueous phase (serum) of the XNBR was determined from contact angle measurements as follows. Latex was dried by ambient temperature evaporation on a PTFE plate to yield a thin (0.5 mm) film. Two 20 x 20 mm

pieces of film were thoroughly washed by immersion in de-ionised water with stirring for 4 days, changing the water each day. The washed films were dried. Serum from the XNBR was generated by freezing a sample of the latex, returning it to room temperature and squeezing the coagulated mass. The liquid-air interfacial tension of the serum was measured using a Krüss K20 EasyDyne (ring method). The contact angle between the serum and the washed film and hence the interfacial tension was measured using a Krüss DSA 30, taking the average of three measurements.

Latex Compounds

As has been reported previously, the properties of nitrile rubber are modified significantly when compounded with zinc oxide, as is the practice in industry.¹⁷ Compounds for dipping were therefore prepared in accordance with this practice, except for the omission of vulcanizing agents, which the previous study showed to have only a minimal effect on wet compound properties.

Compounds were prepared by diluting the base latex with de-ionised water, adding 0.3g of KOH (none for the NR) and 1.0 g of ZnO per 100 g dry polymer, adjusting the compound to pH 9.3 and diluting to 20 wt% total solids content (TSC). The compound was stored at 23°C in a temperature-controlled room for at least 16 hours before use. Three additional compounds were made from the nitrile latex, but with final TSCs of 10, 30 and 40 wt%.

Critical coagulation concentration

The critical coagulation concentration (ccc) of the latex compounds with respect to calcium ions was measured by preparing a series of calcium chloride solutions of different concentrations, then adding a fixed amount of latex compound with stirring. The mix was

filtered and the amount of dry coagulum weighed. The amount of coagulum increased sharply at a particular calcium chloride concentration and this was taken as the ccc of the compound with respect to calcium ions.

Coagulant pick-up

This was measured by placing the coagulant container on a top loading balance. Thus, the weight of coagulant solution transferred to the former for a standard 100 mm dip was obtained. The average of 20 measurements was calculated. This value was used to establish the amount of coagulant to which the latex compound was exposed during (the shorter length) dipping.

The average coagulant pick-up from 20 wt% calcium nitrate solution was found to be 0.018 g dry on the dip area of 0.00292 m². This equates to a coagulant coverage of 6.2 g/m², comparable to the figure of 6.0 g/m² reported by Blackley *et al.*¹⁵ for 20 wt% calcium chloride using glass formers.

Film build-up

A gravimetric method was used, as described previously.¹¹ In brief, a cylindrical stainless steel former was dipped by hand into 20% calcium nitrate at 60°C. The coagulant dip length was controlled at 100 mm through the use of a collar fixed to the top of the former and a fixed weight (= depth) of coagulant solution in its container. After oven drying, the treated former was cooled to 23°C and then hand-dipped into the latex compound, also at 23°C. The compound dip was controlled to a length of 29 mm using the same collar method as for the coagulant.

After the desired dwell time, the former was withdrawn and the film deposit immediately removed. The total solids content (TSC) of the film was determined by simple weighing before and after drying. Dwell times between 2 and

1200 seconds were used in this study. Each experiment was carried out at least in duplicate and the average taken.

From the knowledge of former dimensions, dip length and polymer density, the weights of wet gel and dry film were converted to thickness. The density of XNBR polymer was taken to be 1.0 g.ml^{-1} and that of the NR to be 0.91 g. ml^{-1} . The gravimetric results were corrected for the weight of calcium nitrate, assuming it was all picked up in the film.

It is suggested that this gravimetric method yields a more accurate estimate of the average film thickness than direct measurement, particularly for the very soft, low solids content wet gel samples, as investigated here.

As mentioned, these experiments were carried out at 23°C . This temperature is significantly lower than that commonly used in industrial practice. However, using higher temperatures would introduce serious experimental difficulties with rapid evaporation from the wet gel. There is no obvious way to overcome this problem at present.

Wet Sintering

The dipping procedure used in the investigation of wet sintering was very similar to that described for film build-up. The samples tested were nitrile and natural rubber compounds at 20% TSC. The experiments were carried out at 23°C , with a fixed dwell time of 5 seconds. Immediately after withdrawing the former from the compound, it was inverted and placed vertically on its base. This was sintering time zero. For sintering times greater than ten seconds, the former with wet gel was covered with an aluminium foil sheath, taking care not to touch the sample during the covering process. The sheath was used to minimise water loss by evaporation.

After a measured time, during which the exuded serum ran freely down the film and former towards the base, the polymer film was touched gently with paper tissue to remove surface serum. The film was then removed from the former and its TSC determined as before. Sintering times between 0 and 1200 seconds were used. Each experiment was carried out at least in duplicate and the average taken. As for the film build-up experiment, the results of the wet sintering tests were corrected for the presence of calcium nitrate.

Stress Relaxation

Films were first prepared from 20% TSC compounds by coagulant dipping, using an unglazed rectangular ceramic former. The coagulant was 20 wt% aqueous calcium nitrate and the dipped film was dried at 120°C for 20 minutes. The polymer film was kept in a humidity-controlled atmosphere (23°C , 50% RH) for at least 16 hours before testing.

Dumbbell samples (6 mm width and with the thickness measured in the narrow section) were die-cut from the films and clamped in the jaws of a Hounsfield H10KS-0079 tensiometer. Using purpose-designed instrument software, the sample was rapidly stretched and held at 100% elongation for 10 minutes. The sample stress was measured immediately after elongation and every minute thereafter. At least 3 dumbbells were tested for each polymer and the average taken.

The experiment was repeated for different degrees of elongation, 10, 30 and 50 w%. These experiments were carried out by SATRA Technology Centre Ltd, Kettering, UK, using a SATRA STM 566 tensile testing machine, in a similar manner to that described above.

RESULTS & QUANTITATIVE MATHEMATICAL MODELLING

FILM BUILD-UP

Experimental Results

The experimental results for the evolution of the wet film thickness for the nitrile latex compounds at four different TSCs and the natural rubber compound at 20% TSC are shown in Figure 2. The thickness is that of the wet gel, obtained by calculation from the measured weight and solids content of each dipped sample. It is evident in all cases that the wet gel thickness increases rapidly at first, and then slows down to a growth rate of approximately zero. It is noticeable that at short dwell times, perhaps less than thirty seconds, all five samples have a remarkably similar wet gel growth rate. For the nitrile series, the rate reduction is more marked as the compound TSC increases. At 20% TSC, the growth rate reduction appears to be slightly more marked for the nitrile than for the natural rubber.

Analysis of the Results and Quantitative Modelling

Table 1 shows the values of the parameters needed in the calculations. These were obtained by the experiments described earlier and from the literature.

Simple diffusion

Earlier studies assume that the dominant effect driving film build-up in coagulant dipping is the diffusion of coagulant-derived material, normally calcium ions. The build-up model presented here uses coagulant diffusion as the main mechanism, on the basis of previous published evidence and the absence of an obvious alternative.

As a model we take a flat plane of calcium nitrate coagulant. At time zero, diffusion of the calcium

and nitrate ions into an infinite bath of latex begins. Fick's second law can be used to derive an analytical expression for the coagulant ion concentration, c , as a function of the distance x from the source plane and time, t . This expression is shown as Equation (1).

$$c = c_0 \left(1 - \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right) \quad (1)$$

The derivation is subject to a fixed coagulant concentration c_0 at the plane boundary, a zero coagulant concentration at large distance from the plane and the latex initially being free of $\text{Ca}(\text{NO}_3)_2$ coagulant. We have assumed that c_0 is the saturation concentration of $\text{Ca}(\text{NO}_3)_2$ in water at 23°C. The parameter D is the diffusion coefficient of the ions in the latex. The function erf is called the error function and its values are readily available in tables.²⁵

When the calcium ion concentration is above a particular level, the critical coagulation concentration, c^* , the latex will begin to aggregate. For the diffusion discussed here, a moving aggregation front occurs at the point where c becomes equal to c^* . The thickness of the zone where aggregation has occurred therefore increases with time as diffusion proceeds. We write this thickness as L and from equation (1) it is given by

$$L = \sqrt{4Dt} \operatorname{erf}^{-1} \left(1 - c^*/c_0 \right) \quad (2)$$

where erf^{-1} is the inverse error function. This is the basic equation for the thickness of the wet gel as a function of time. As can be seen, it depends on the diffusion coefficient of the coagulant ions, the critical coagulation concentration of the latex with respect to Ca^{2+} (c^*) and the concentration of Ca^{2+} at the former

(c_0), which is assumed at this stage to remain constant. The build-up rate calculated using the values of these parameters (shown in Table 1), compared to the experimental results for the five latex compounds is shown in Figure 3.

It is evident that the simple diffusion model gives a good fit to the wet gel build-up for both the nitrile and natural rubber compounds at short dwell times. The insert in Figure 3 shows the close agreement with the simple diffusional model up to 30 seconds. This is strong support for the long-held assumption that film growth is governed by diffusion. At later times the experimental values depart increasingly strongly from the diffusional model, showing a reduction in build-up rate. Rate reductions at longer dwell times were also noted in other work,¹⁴⁻¹⁶ although Blackley ascribed the rate reduction to an experimental artefact.

We now explore possible reasons for the reduction in build-up rate at longer dwell times, as found in our experiments.

1. Diffusion with tortuosity.

As latex particles flocculate to form the wet gel, the path that coagulant ions have to take to reach the coagulating front becomes more tortuous. In addition, the area for diffusion decreases, reducing the flux of coagulant. Both Stewart¹⁴ and Blackley¹⁵ mentioned this idea. The usual way to model tortuosity is to reduce the diffusion coefficient by a factor T , which is the extra distance that the solute must travel because of the convoluted path. According to Cussler,¹⁸ typical values for the tortuosity (defined as tortuous path length/straight path length) are between 2 and 6, although values as large as ten have been measured.

Figure 4 shows the predicted wet film thickness using equation (2), but with D modified by three different values of T , covering the range

mentioned by Cussler. The simple diffusion case, with an unmodified D value, of course corresponds to $T = 1$. Figure 4 also shows the experimental results (plotted as points) for the 20 wt% natural rubber and nitrile compounds.

As can be seen, despite their wide range, none of these tortuosity values gives a build-up profile that corresponds to that obtained experimentally throughout the experimental timescale. At short dwell times, the best fit is obtained using $T = 1$, i.e. no tortuosity, which is perhaps to be expected. At long dwell times, the greatest T gives the best fit, but with a curve that does not follow the shape of the experimental points.

According to Dias *et al.*,¹⁹ the tortuosity of a low density array of particles is found to depend weakly on the particle volume fraction ϕ as $T \sim 1/(1-\phi)^n$, where n has a value between 0.4 and 0.5. For our system the particles are deforming, so a sphere packing model is not strictly applicable. However, as will be seen later with the wet sintering results, the average particle volume fraction in the wet gel from the 20% compounds only increases from around 0.2 to 0.3 in the 20-minute experimental period. This means the value of the tortuosity is not expected to change significantly. Using the Dias relationship and volume fraction values from all five compounds indicates that T values of significantly less than 2 are likely. Figure 4 shows that this tortuosity would not play a major part in moderating the coagulant flux and hence film growth, at least in the compounds examined here.

2. Diffusion with surfactant reaction

Another possibility for a reduction in Ca^{2+} flux through the wet gel, is precipitation by reaction with the anionic surfactant used to stabilise the latex. This mechanism was rejected by Blackley,¹⁵ but was used by Stewart¹⁴ as a

method of calculating the amount of Ca^{2+} needed to coagulate the latex.

Although little data is available in the literature for the kinetics of the reaction of Ca^{2+} with surfactants, some rate curves have been published for sodium dodecyl sulphate (SDS) and sodium octylbenzene sulphonate (SOBS),²⁰ which are surfactants similar to those used in the nitrile latex, and for sodium laurate.²¹

To account for this reaction in a mathematical model, it is necessary to consider its kinetic order. Unfortunately, it is difficult to decide this from the published work, which was designed to investigate precipitation. The approach we take is to assume the two most likely possibilities, first order and second order. The kinetic equations for each of these orders are applied to the published data, to calculate the rate constants for the Ca^{2+} - surfactant reaction. These are then compared with the rate constants needed in our model to fit the experimental data. It is worth remembering, however, that the published work dealt with precipitation kinetics, which may differ from the kinetics of Ca^{2+} consumption.

Reaction assuming pseudo first order reaction kinetics

Intuitively, we might expect the reaction to depend on both the surfactant and Ca^{2+} concentrations. However, at the coagulating front, there is a low Ca^{2+} concentration moving into fresh compound serum containing a higher (about 4x) molar concentration of surfactant. Therefore, there is a potentially large supply of surfactant available from the latex, which would lead to a constant surfactant concentration and pseudo first order kinetics. In this scenario we expect a rate constant that depends on the surfactant concentration in the compound. The first order rate constant of the Ca^{2+} - surfactant reaction estimated from the data provided in the Rodriguez and Clarke papers,^{20, 21} was between

0.01 and 0.23 sec^{-1} . There is no equivalent published data for the phospholipid/protein stabilisers in natural rubber, so at this stage it was assumed that they react with Ca^{2+} in a similar way and with a similar rate.

Turning to the model, as a first approximation we modify the diffusion equation for the coagulating front by considering an additional term that accounts for the loss of Ca^{2+} through a first order reaction with the surfactant. The modified equation can only be solved by computational means and the methodology is shown in Appendix 1. The treatment requires the introduction of the Damköhler number, which is the ratio of the rate of loss of Ca^{2+} to its rate of diffusion.

The results of the solution to the diffusion-reaction equation, EA2, for various values of the Damköhler number are shown in Figure 5, together with the experimental results for both the nitrile and natural rubber at 20% TSC. Since we know the diffusion coefficient, D , using various values for the Damköhler number is essentially testing different values for the reaction rate, k . Figure 5 shows that choosing k in the reaction-diffusion equation can produce a curve for the build-up of wet gel that is very similar to the experimental results throughout the dwell time range used in the experiments. The best fit is given for a Damköhler number of 0.5 to 1, corresponding to reaction rate constants of 0.025 and 0.05 s^{-1} . These values lie within the range of the estimates from the published work, supporting the idea of coagulant reaction with (pseudo) first order kinetics.

Reaction assuming 2nd order reaction kinetics

As mentioned above, we might expect that the surfactant- Ca^{2+} reaction would depend on the concentrations of both these species, i.e. second order kinetics. Using the same published data as before, but applying second order kinetic

equations, the second order rate constant was estimated from the data of Rodriguez et al.²⁰ to be $3.1 \text{ M}^{-1} \text{ s}^{-1}$.

Assuming second order kinetics changes the governing equation for the coagulant diffusion as shown in Appendix 2. A single dimensionless group, the ratio of initial concentrations of surfactant to coagulant, p_0/c_0 , controls the profile. This is a result of assuming that the supply of Ca^{2+} ions to the reaction site is controlled by diffusion from the former face and the supply of surfactant anions is controlled by diffusion from the bulk compound with the same diffusion rate. Numerical solutions are shown in Figure 6, where it can be seen that a value of p_0/c_0 of around 1 provides predictions for the film thickness that are the right magnitude, although a good fit to the experimental data throughout the dwell time range is not found for any value. In addition, the known values of p_0 , the concentration of surfactant in the compound serum and c_0 , the saturation concentration of calcium nitrate in water, for these experiments, produce a p_0/c_0 value of 0.004, obviously far removed from unity. Solutions for p_0/c_0 values of 0.004 in Figure 6, are indistinguishable from the diffusion solution.

Consequently we conclude that 2nd order reaction alone cannot explain the observed slowdown in film thickness growth. On the basis of the data currently available, we see that pseudo first order kinetics gives a better fit to experiment than second order kinetics.

3. Diffusion with a finite amount of coagulant.

The third mechanism for the observed reduction in build-up rate acknowledges that in normal coagulant dipping, there is a finite amount of coagulant available to diffuse into the latex. For the present study, this amount was reported in the Materials & Methods section.

There being a finite amount of coagulant leads us to relax the assumption that the coagulant concentration at the former (c_0) is constant throughout the dwell time. It is possible to devise a model for the case of a finite quantity of coagulant as shown in Appendix 3. The result of applying this model is shown in Figure 7. As might be expected, we find that a limited amount of coagulant reduces the rate of film build-up, but the reduction on its own does not account for the experimental observations.

The effect of different Total Solids Contents

We have seen that the experimental results for the nitrile compound series show that the second-stage rate reduction is more marked as the compound TSC increases. It is interesting to consider how each of the three mechanisms described above could explain this.

The tortuosity of the wet gel will increase with increasing compound TSC. However, as discussed above, calculations (not shown) using the Dias tortuosity expression for the TSC range 10 to 40 wt% show that this effect is small and much less than is observed experimentally. In addition, any significant effect of TSC on tortuosity and diffusional cross sectional area should be evident at shorter dwell times, whereas no effect is found experimentally.

The limited coagulant effect should apply equally to all four compounds, so this does not explain the differences in rate reduction that are observed.

Turning to the surfactant reaction mechanism, since all the surfactant in these compounds comes from the latex, the concentration of surfactant increases approximately in proportion to the compound solids content. Assuming pseudo first order kinetics, increasing the surfactant concentration will serve to increase the pseudo first order rate constant. As

shown in Figure 8, the 20 wt% compound fits well using a Damköhler number of about 1. Since the Damköhler number is directly proportional to the concentration of surfactant, the Damköhler number for the 10, 30 and 40% TSC compounds can readily be calculated. We find that at 10%, the Damköhler number is 0.44, at 30% it is 1.71 and at 40% it is 2.66.

Incorporating these Damköhler numbers into Equation EA2, we obtain the results shown in Figure 8. We see that the predicted changes in build-up from surfactant concentration change are in reasonable agreement with the experimental film thicknesses from the nitrile TSC series, giving support to the pseudo first order surfactant reaction mechanism.

Combining finite amount of coagulant with 1st order reaction kinetics.

The analysis above suggests that the effect of tortuosity is small, but that both surfactant reaction and a limited total supply of coagulant have to be considered.

So finally, we combine the effect of limited amount of coagulant and 1st order reaction. From Appendix 2, the equation to solve is:

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - Da c \quad (3)$$

where time has been scaled on t^* and distance on x^* , with the relation $x^* = \sqrt{Dt^*}$.

At early times, when there is still coagulant on the former the boundary conditions are

$$\begin{aligned} x = 0 & \quad c = c_0 \\ x \rightarrow \infty & \quad c \rightarrow 0 \\ t = 0 & \quad c = 0 \end{aligned} \quad (4)$$

After a time, t_{diss} , the coagulant has all dissolved into solution and the boundary conditions become

$$\begin{aligned} x = 0 & \quad \frac{\partial c}{\partial x} = 0 \\ x \rightarrow \infty & \quad c \rightarrow 0 \end{aligned} \quad (5)$$

Using equation EA11 and the parameters in Table 1 one obtains a value of $t_{diss} = 0.08$ seconds. This is much smaller than the time for dipping. We therefore make the assumption that the concentration profile at $t = t_{diss}$ follows the error function solution and then solve equation (3) subject to boundary conditions (5) for times greater than t_{diss} , i.e. all times for which experimental results were obtained. The result for the thickness of the film as a function of time is given in Figure 9. The single experimental parameter is the Damköhler number, Da , which is simply the dimensionless form of the 1st order rate constant.

Comparing Figure 9 with Figure 5 one can see that for a given value of Damköhler number the predicted film thickness is reduced by the effect of limited coagulant, but the effect is not dramatic.

In Figure 9, we see that the 20% natural rubber & nitrile experimental points can be fitted to the combined effect curves at Damköhler numbers in the range of 0.1 and 0.2, lower than the values of about 0.5 and 1 found for the surfactant-only case. This is a reflection of the fact that with the combined effects, we need slightly smaller rate constants for the surfactant reaction in order to match the experimental results.

WET SINTERING

Experimental Results

The results for latex particle size and nitrile polymer-serum interfacial tension are included in Table 1, and were used as parameters in the wet sintering modelling calculations. The other parameters needed in the calculations were

obtained from the literature and are also shown in Table 1.

As will be discussed later, modelling the wet sintering process requires knowledge of the stress relaxation modulus of the polymer. The experimental stress relaxation data for the various applied strains are shown as the points plotted in Figure 10 for the nitrile latex and Figure 11 for the natural rubber. Both materials display a plateau in residual elasticity and both have a lower modulus at higher applied strains. This implies that the assumption of linear viscoelasticity will become less accurate at higher strains.

Note that each set of data points shown in the Figures are from one particular experiment. At least three repeat stress relaxation experiments were carried out for most of the samples and the average used in the data analysis described later.

The points in Figures 12 and 13 show the experimental average wet gel volume fraction for the 20 wt% nitrile and natural rubber compounds as a function of different sintering times. For the nitrile, the volume fraction increases from 0.21 to 0.33 over a timescale of 20 minutes. The data for the natural rubber show a similar result, with the volume fraction increasing from 0.23 to almost 0.30 over 20 minutes. It is noticeable how, for both dispersions, the average volume fraction seems to reach a plateau. This indicates a stress balance has been achieved within the film and that the particles are displaying an elastic behaviour under the wet sintering conditions.

We can see in Figures 12 & 13 that the volume fraction of polymer in the wet gel, just after withdrawal from the dipping bath, is at a value close to that of the host compound. It then increases by about 40 – 50% during the next 100 seconds. After this, there is little or no further

increase. The cause of this volume fraction increase and a mathematical model are discussed below.

Analysis of the Results and Quantitative Modelling

As mentioned earlier, the presence of calcium ions above the critical coagulation concentration causes the polymer particles to come into irreversible contact, forming a continuous matrix. The finding that the matrix and compound volume fractions are similar suggests that the film deposition process is one of phase inversion at approximately the solids content of the latex compound. Once the particles come into contact, they undergo wet sintering through the driving force of the polymer-water interfacial tension. The local volume fraction increases, expelling liquid serum from the wet gel and producing the phenomenon that is observed in practice as syneresis. The rate and amount of syneresis therefore depends directly on the extent of wet sintering.

The relatively recent work of Routh and Russel⁹ can be used to model the wet sintering process. In contrast to the Stewart paper, where the calculation was limited to the deformation of two discrete particles, this model considers an array of particles. This approach requires a mathematical description of the rheological behaviour of the polymer particles. This can be derived from the relaxation modulus, measured as described above. There are an infinite number of possible rheological models that might be used to analyse the stress relaxation data. Intuitively, we expect that for elastomers such as natural rubber and nitrile rubber, a viscoelastic solid model would be appropriate. For this model, the stress relaxation modulus is given by:²²

$$G(t) = G_1 + G_2 \exp\left(-\frac{G_2 t}{\eta}\right) \quad (6)$$

where G_1 is the long time residual modulus, η is the polymer viscosity and $(G_1 + G_2)$ is the early time modulus. Within such a model, the modulus has a finite long time value and a single relaxation time.

The experimental stress relaxation data were fitted to equation (6), yielding values for G_1 , G_2 and η . The best fits are shown as lines in Figures 10 & 11.

The parameters G_1 , G_2 and η , obtained by fitting all the stress relaxation curves for both polymers are shown in Table 2. In addition, the time constant, τ , defined as $\tau = \eta/G_2$ is included in Table 2. This is the typical relaxation time for the polymer.

It should be noted that the rheological parameters reported here are from measurements on a dry film, whereas the wet sintering deformation occurs in a wet environment. For the relatively hydrophobic natural rubber, the film modulus probably provides a reasonable measure of the sintering modulus. In contrast, the nitrile latex contains a significant amount of hydrophilic groups, which may promote some water absorption, possibly reducing the sintering modulus. However, as discussed elsewhere,¹⁷ the Zn^{2+} , provided by added ZnO, neutralises and possibly crosslinks the hydrophilic units in the wet state, which will tend to reduce water absorption. It is suggested, therefore, that the dry film relaxation modulus is probably the best estimate of sintering modulus we can provide at this stage.

The rate at which the local volume fraction increases depends on the driving force for sintering – in this case the polymer-water interfacial tension, γ , divided by the original particle radius, R_0 – and the rheological response

of the polymer particles. Routh and Russel derived the following equation to describe this:⁹

$$\frac{14}{5} \frac{\gamma}{R_0} \varepsilon = \int_0^t G(t-t') \frac{d\varepsilon^2}{dt'} dt' \quad (7)$$

Their model is kept general by writing the mechanical response to the sintering force as the stress relaxation modulus $G(t)$. In equation (7), ε is the local strain in the film.

This model calculates the rate of the dimension change (as given by the strain) in the consolidating film, assuming the polymer behaves according to linear viscoelasticity. Consequently, the mechanical response of the material at time t is dependent on the strains at all previous times, t' . Once $G(t)$ is known, equation (7) can be solved and the strain follows as a function of time. Inserting the expression for $G(t)$ given by equation (6) into equation (7) we obtain a differential equation for the strain in the film:

$$\frac{14\gamma}{5R_0} \left(\varepsilon + \frac{\eta}{G_2} \frac{d\varepsilon}{dt} \right) = G_1 (\varepsilon^2 - \varepsilon^2(0)) + \frac{\eta}{G_2} (G_1 + G_2) \frac{d\varepsilon^2}{dt} \quad (8)$$

For the wet sintering problem, we have values for every parameter in equation (8), except for the strain to be used for the stress relaxation modulus.

The stress relaxation experiments provided modulus values for a reasonably wide number of strains (10, 25, 50 & 100%). It can be seen, from Table 2, that for the polymers used here, the modulus depends strongly upon strain.

As stated previously, the 5 seconds dwell time in the wet sintering experiments is much shorter

than a typical time for deformation. This means that the film deformation can be taken to be homogeneous and the strain ε can be regarded as having a single value at any given time.

The predictions obtained from equation (8) for the volume fraction as a function of wet sintering time using the experimental strain and modulus values are shown in Figures 12 and 13. For comparison, the measured volume fraction data are also shown. As can be seen, the experimental results for both polymers are found to lie between the model results for strains of 50 to 100%.

The question then arises – what value of strain do we expect for the wet sintering process? Since the wet gel is not able to contract along the former and can only collapse towards it. Using an overall mass balance we estimate that the strain ε is related to the volume fraction, ϕ , and original volume fraction, ϕ_m by the equation:

$$\phi = \frac{\phi_m}{1 - \varepsilon} \quad (9)$$

So from the experimental volume fraction changes, we estimate the maximum ε value for nitrile is $\sim 36\%$ and for NR is $\sim 23\%$.

These values are somewhat lower than the 50 to 100% required to fit the model to experiment, but perhaps reasonably close considering the uncertainty in the modulus and the sensitivity of the model to it.

Wet Gel Volume Fraction During Dipping

An additional piece of information that comes from the film growth (dwell time) experiments is the average volume fraction of polymer in the wet gel *during* immersion. In this stage of the process, film growth and particle deformation occur concurrently, but, as mentioned previously with the deformation being much the slower process. Significant change in wet gel

volume fraction during immersion is therefore likely only to occur at long dwell times. Dwell times of 5 to 20 minutes as used in some of the present experiments are not practised industrially in thin glove manufacture, so the results in this section have less practical relevance. However it is interesting to compare the theory and experimental measurements. We assume that the film growth follows a diffusional model. This enables a simple expression for the film thickness to be used and avoids complicating the analysis with too many parameters. It is, of course, fairly easy to use any of the film growth models above and couple this to the wet sintering model.

Experimental Results

The symbols in Figures 14 and 15 show the experimental average volume fraction during dipping for the 20% compounds of the two polymer types. The average wet gel volume fraction for both polymers was found to increase with time with a rate that decreased with time, in a broadly similar way to the simple case of wet sintering described above. For the nitrile latex (Figure 14), the volume fraction increases from 0.23 up to 0.29 in 20 minutes. The natural rubber values, shown in Figure 15, increases from 0.22 to about 0.26 in 20 minutes.

Analysis of the Results and Quantitative Modelling

The experiments described here enable the polymer volume fraction during immersion in the compound to be measured. Since we have modelled both build-up and wet sintering separately, it is an interesting challenge to combine the models to calculate values for this volume fraction and compare these to experiment.

To do this, it is useful to convert the build-up process as described in equation (1) to the time domain. We can say that the time the flocculating front passes through distance x in the latex compound is t^* , which is the time the sintering, at this spatial position, starts. t^* is given by the solution for L given in equation (2), hence

$$t^* = t - \frac{1}{4D} \frac{x^2}{\left(\operatorname{erf}^{-1} \left(1 - c^*/c_0 \right) \right)^2} \quad (10)$$

The average volume fraction in the consolidated region on the mould is then given by averaging over the entire consolidated region.

$$\hat{\phi} = \frac{1}{L(t)} \int_0^{L(t)} \phi dx \quad (11)$$

Solving equation (8), within the collapsing film model described by equation (10) results in a range of strains and consequently volume fractions across the film. These can be averaged, using equation (11) to provide the average film volume fraction. A useful check is that the final value of the strain in the film is given by the solution to equation (8), when the time derivative terms are set to zero. Alternatively, the strain is determined by the driving force (γ/R_0) balancing the long-time modulus G_1 . The final value of the strain is given by $\varepsilon \sim 14 \gamma^{1/5} R_0 G_1$.

The line in Figure 14 is the predicted average nitrile film volume fraction using the wet sintering model within a consolidating film as outlined in equations (8) – (10). Again it should be noted that all parameters are measured and

the stress relaxation modulus is taken at a strain of 50%. Figure 14 also shows the experimental results. It can be seen that the calculated values are close to those measured experimentally.

Figure 15 shows the predicted average volume fraction compared to the experimental results for the natural rubber sample. Here there is a greater discrepancy between the calculated and experimental results, perhaps due in part to the unexpected decrease in experimental volume fraction at short dwell times.

There is no obvious physical reason for such a decrease, so this observation is provisionally attributed to some small experimental error.

SUMMARY AND CONCLUSIONS

This paper reports a detailed examination of the rate of film build-up and rate of wet sintering in coagulant dipped films. The approach is to construct mathematical models of the two processes and compare the results with experimental data. The latexes used were nitrile and natural rubber. For both polymers, the values of parameters (or similar parameters) needed for the models were available from the literature or were measured. The temperature pertaining to the experimental data and the model parameters was 23 - 25°C, acknowledged to be less than that of commercial dipping.

The first stage (0-30 seconds) of the dipping process was a rapid build-up of wet gel. The rate of this initial build-up was very similar for all the compounds reported. A relatively simple model based on standard diffusion equations successfully predicted this initial build-up. It is remarkable that using only three known or measured parameters, the weight/thickness of dipped films from a variety of compounds could be calculated with good accuracy. This strongly

supports the diffusion mechanism of film build-up.

According to the diffusion equation, the parameters that control film build-up are the diffusion coefficient of the coagulant ions, the critical coagulation concentration of the latex with respect to the coagulant and the concentration of Ca^{2+} at the former. Of these, the diffusion coefficient term is dominant. This is consistent with the experimental finding that the initial build-up rate of wet gel does not change significantly with compound type. This rate would also be expected to apply to other compounds. Note that the constant initial rate applies to the wet gel thickness. Of course, for compounds of different solids contents, the dry film build-up will be scaled proportionately.

After 30 seconds dwell, the build-up of wet gel was found to decrease quite sharply, something not predicted by the simple diffusion model. The reason for this slow down must be a reduction in the flux of coagulant ions reaching the wet gel - liquid compound interface. Three reasons for reduced flux were considered; the increasing tortuosity and reduced diffusional cross section provided by the wet gel through which the coagulant ions diffuse, precipitation of the coagulant cations with surfactant anions and the finite supply of coagulant available from the former surface. Calculations were performed, separately modifying the simple diffusion equation with terms to account for each of these effects.

Using an accepted relationship between diffusion, tortuosity and volume fraction in dispersed systems, the effect of wet gel tortuosity on diffusion rate was calculated to be small for the compounds studied. Including high (and therefore unlikely) tortuosity values failed to provide build-up curves of the same shape as those found experimentally. Furthermore, the wet sintering data show that polymer volume

fraction (and hence expected tortuosity) increases relatively slowly over 1200 seconds, whereas the observed reduction in film build-up occurs quite suddenly after 60 seconds. The initial film build-up rate was found to be independent of TSC for the compounds investigated here. These observations strongly suggest that the effect of cross-sectional area on coagulant diffusion was small. It is concluded, therefore, that wet gel tortuosity and diffusional cross sectional area are not major factors in limiting coagulant flux.

The effect of reaction between surfactant and coagulant (calcium ions) was examined with the outcome that pseudo first order kinetics could predict the build-up rate throughout the large dwell time range covered by the experimental results. The correspondence between model and experiment depends greatly on the Ca^{2+} - surfactant reaction rate constant (k) used. k values were obtained from data in the literature for similar, although not identical surfactants. Establishing the kinetics for the reaction of suitable surfactants with calcium ions could usefully be the subject of future work.

The finite amount of coagulant available in the dipping process was calculated to reduce the rate of film build-up as expected, but the effect was not as great as that of surfactant reaction. Nevertheless, since we know that there is only a finite amount of coagulant available, this mechanism must be present. In fact, this is the only obvious reason for the practical observation that coagulant concentration (and hence the amount of coagulant on the former) has an effect on latex film thickness. The calculations also suggest that the coagulant completely enters the wet gel surprisingly quickly (<1 sec., see Appendix 3).

The results presented here indicate that the moderation in build-up rate is mainly due to coagulant reaction with surfactant. Although

the build-up of the natural rubber latex was broadly similar to that of the nitrile, its slow-down is not as marked at similar compound solids contents. This, therefore, has to be attributed to the different types of surfactant in the natural rubber latex.

Modelling the wet sintering process presented several problems. The mathematics of calculating the rate of polymer particle coalescence, moderated by the viscoelastic properties of the polymer, is not trivial but is possible. It requires knowledge of the stress relaxation modulus, which depends strongly on the strain (elongation) that is imposed on the polymer during wet sintering. Moderate agreement between model and experiment was obtained. To progress this model, more work on the polymer rheology in the wet compound state would be required.

In addition, the coalescence model of wet sintering requires knowledge of the particle radius of the latex, which is straightforward for the fairly monodisperse nitrile, but not so for the polydisperse natural rubber. There is no obvious solution to this difficulty.

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Appendix 1: Diffusion and 1st order reaction into an infinite medium

For the case of diffusion with a 1st order reaction, the partial differential equation to solve for the concentration profile of Ca^{2+} ions becomes

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - kc \quad (\text{EA1})$$

where k is the (assumed) first order rate constant for the reaction. The boundary conditions are a fixed concentration, c_0 at the former surface, ($x=0$) and a zero concentration at great distance ($x \rightarrow \infty$). No analytic solution to equation EA1 exists and so we proceed with a numerical solution. To achieve this we scale distances with a characteristic distance X . The characteristic time, t^* , follows as $t^* = X^2/D$ and the problem becomes dependent on a single dimensionless group, the Damköhler number, which measures the rate of reaction compared to the rate of diffusion. In scaled form equation EA1 becomes

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - Da c \quad (\text{EA2})$$

where the Damköhler number, Da is defined by $Da = kX^2/D$. Solutions to equation EA2 are readily

obtained in Mathematica using a finite difference approach and a simple Euler time step. Solutions (in dimensionless form) are shown in Figure A1.

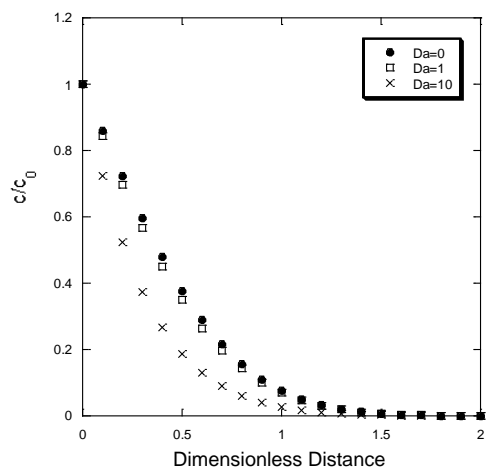


Figure A1: Graph of concentration versus distance from plate at a time of 0.15 sec for various values of the Damköhler number.

Appendix 2: Second order reaction between coagulant and surfactant

If we assume that the coagulant and surfactant react via a second order reaction then we introduce the concentration of surfactant as p . The partial differential equations governing the evolution of coagulant and surfactant concentrations become

$$\frac{\partial c}{\partial t} = D_{\text{salt}} \frac{\partial^2 c}{\partial x^2} - kcp \quad (\text{EA3})$$

$$\frac{\partial p}{\partial t} = D_{\text{surf}} \frac{\partial^2 p}{\partial x^2} - 2kcp \quad (\text{EA4})$$

Where D_{salt} is the diffusion coefficient of the coagulant, D_{surf} is the diffusion coefficient of the surfactant and the factor 2 appears in equation EA4 because one calcium ion reacts with two surfactant molecules. The boundary conditions on equations EA3 and EA4 are a coagulant concentration of c_0 at the plate boundary and zero at large distance. For the surfactant the opposite applies with a fixed initial value at large distance and a value of zero on the plate

For simplicity we assume that the diffusion coefficients are the same, $D_{\text{surf}} = D_{\text{salt}} = D$. To non-dimensionalise the equation we use the plate coagulant concentration c_0 and the initial, uniform surfactant concentration in the compound serum, p_0 . We scale time with an unknown timescale t^* and distances with a distance L . To satisfy the similarity solution we insist that $t^* = L^2/D$ and to balance reaction and diffusion we set $k c_0 t^* = 1$. The resulting equations are

$$\frac{\partial \bar{c}}{\partial \bar{t}} = \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - \frac{p_0}{c_0} \bar{c} \bar{p} \quad (\text{EA5})$$

$$\frac{\partial \bar{p}}{\partial \bar{t}} = \frac{\partial^2 \bar{p}}{\partial \bar{x}^2} - 2\bar{c} \bar{p} \quad (\text{EA6})$$

With boundary and initial conditions

$$\begin{aligned} \bar{x} = 0 & \quad \bar{c} = 1; \bar{p} = 0 \\ \bar{x} \rightarrow \infty & \quad \bar{c} = 0; \bar{p} = 1 \\ \bar{t} = 0 & \quad \bar{c} = 0; \bar{p} = 1 \end{aligned} \quad (\text{EA7})$$

Where the overbar donates a dimensionless quantity. The value for the second order rate constant is estimated from the data of Rodriguez *et al* to be $3.1 \text{ M}^{-1} \text{ s}^{-1}$. Using the parameter values in Table 1, the time and length scales are given by

$$t^* = \frac{1}{k c_0} \sim 0.061 \text{ s} \quad (\text{EA8})$$

$$L = \sqrt{\frac{D}{k c_0}} \sim 5.5 \times 10^{-6} \text{ m} \quad (\text{EA9})$$

To enable numerical solutions to be obtained in reasonable times, the characteristic concentration was chosen to be $c_0/100$. This allows the timescale to increase to 6.1 seconds and the characteristic length scale to be $5.5 \times 10^{-5} \text{ m}$.

In the scaled form the solution is dependent on the single dimensionless group, p_0/c_0 . For the case of $p_0/c_0 = 0$, the solution reverts to the diffusion only case. From a knowledge of the nitrile latex composition and the solubility of calcium nitrate, we obtain values for $p_0 = 0.022 \text{ M}$ and $c_0 = 5.3 \text{ M}$, resulting in a value of p_0/c_0 of 4×10^{-3} , which is $\ll 1$.

Solutions are obtained numerically, again using finite differences spatially and a simple Euler time step. As expected, the size of the wet film thickness decreases as the amount of reaction is increased. This is shown in Figure 6, although it is noticeable that for the experimental value of

p_0/c_0 of 4×10^{-3} the numerical curves do not match the experimental points.

Appendix 3: limited amount of coagulant

The total amount of coagulant on the former in the dipping area is taken as S . At early times the concentration profile of coagulant in solution is given by the error function solution, equation (1). Taking the dipping area of the former as A , the total amount of coagulant in solution is given by

$$Ac_0 \int_0^{\infty} \left(1 - \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right) dx = Ac_0 \sqrt{Dt} \frac{2}{\sqrt{\pi}} \quad (\text{EA10})$$

Balancing the amount of coagulant in solution with the total amount of coagulant available determines the time of complete dissolution, t_{diss} as

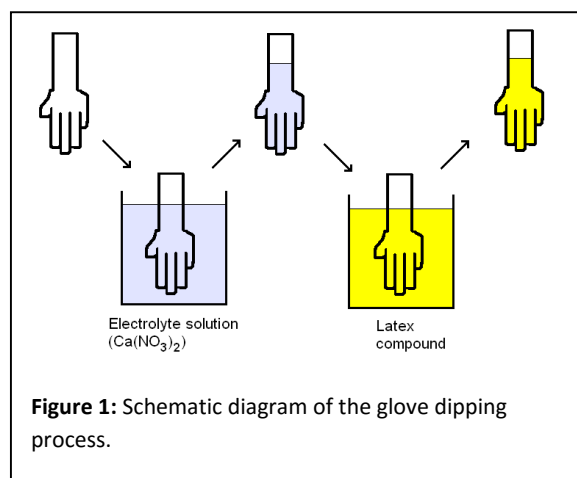
$$t_{\text{diss}} = \left(\frac{S}{2Ac_0} \right)^2 \frac{\pi}{D} \quad (\text{EA11})$$

Using equation EA11 and the parameters in Table 1, one obtains a value of $t_{\text{diss}}=0.08$ seconds.

For times less than t_{diss} the coagulant profile follows the error function solution (equation 1), for times greater than t_{diss} , the boundary condition at the former ($x=0$) changes from a constant concentration, to one of zero flux, $dc/dx = 0$. The zero flux condition arises because of the depletion of electrolyte and so no more salt flowing into the system across the boundary at $x=0$.

The resulting wet film thickness is plotted in Figure 7. The experimental points for both the nitrile latex and the natural rubber are included in the Figure. It is noticeable that, although the finite coagulant model is closer to the experimental measurements the agreement

with experiment at longer dwell times is not good.



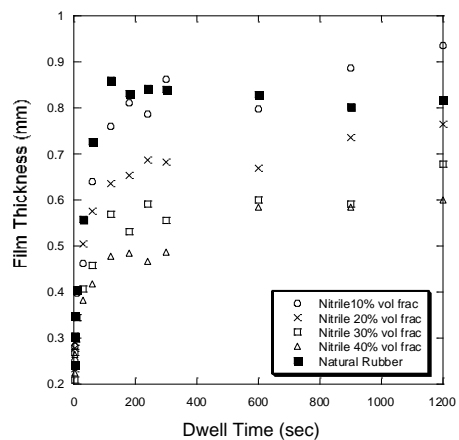


Figure 2 : Film Build-Up for Nitrile & Natural Rubber Samples.

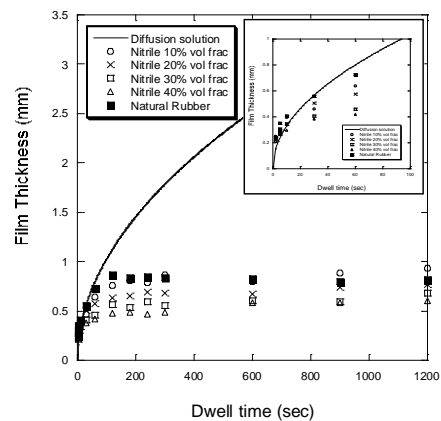


Figure 3: Film thickness for various total solids contents and the model for simple diffusion. The inset shows the data for the first 100 seconds.

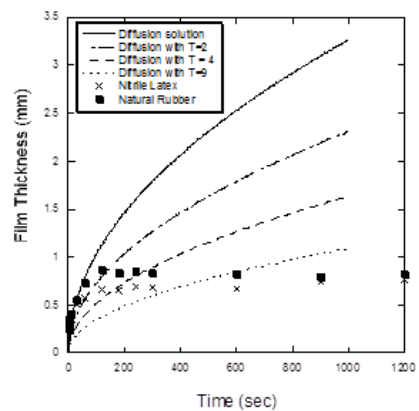
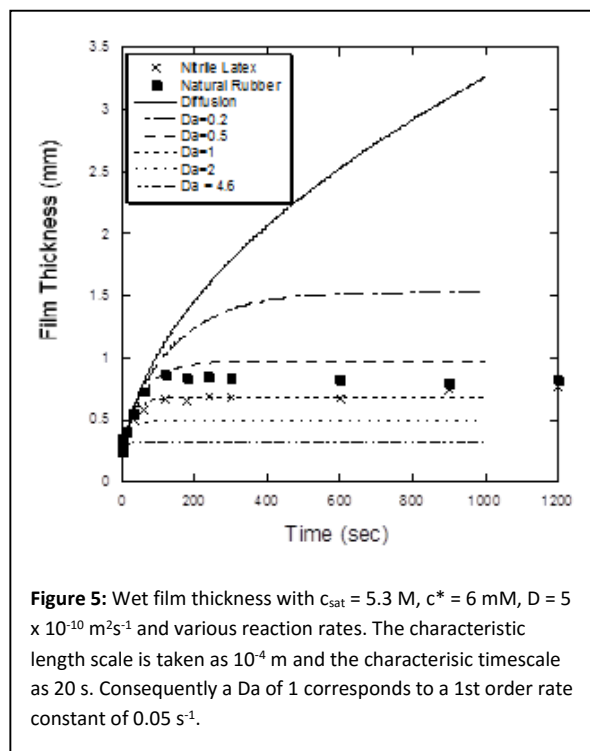


Figure 4: Wet film thickness using diffusion and a tortuosity model where the diffusion coefficient is reduced by the tortuosity. For this model the value of $c_{\text{sat}} = 5.3 \text{ M}$, $c^* = 6 \text{ mM}$, and $D = 5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$. The experimental results for 20% nitrile and 20% natural rubber compounds are shown for comparison.



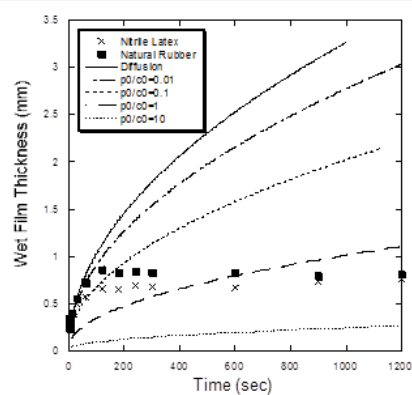


Figure 6: Dimensionless wet film thickness versus dimensionless time for various values of the single controlling dimensionless group, p_0/c_0 . The second order rate constant is taken as $3.1 \text{ M}^{-1}\text{s}^{-1}$ and consequently the time constant is 0.06 s and the characteristic distance is 5.5 mm .

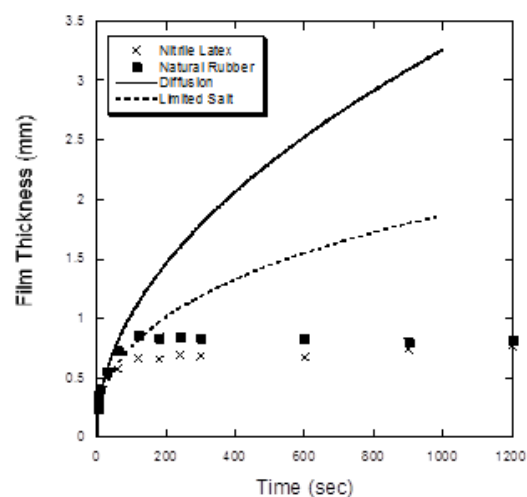


Figure 7: Wet film thickness using the model for a limited amount of coagulant as described in appendix 4. The total amount of coagulant on the former was taken as the measured amount of 0.00011 mol, $c_{\text{sat}} = 5.3$ M, $c^* = 6$ mM, and $D = 5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$.

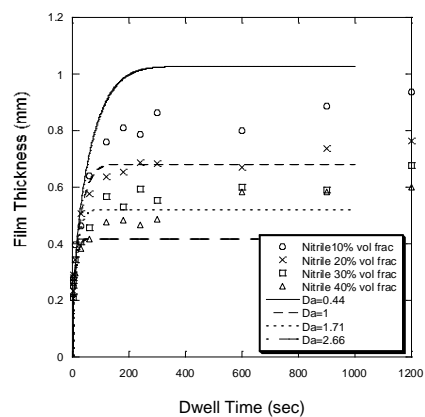
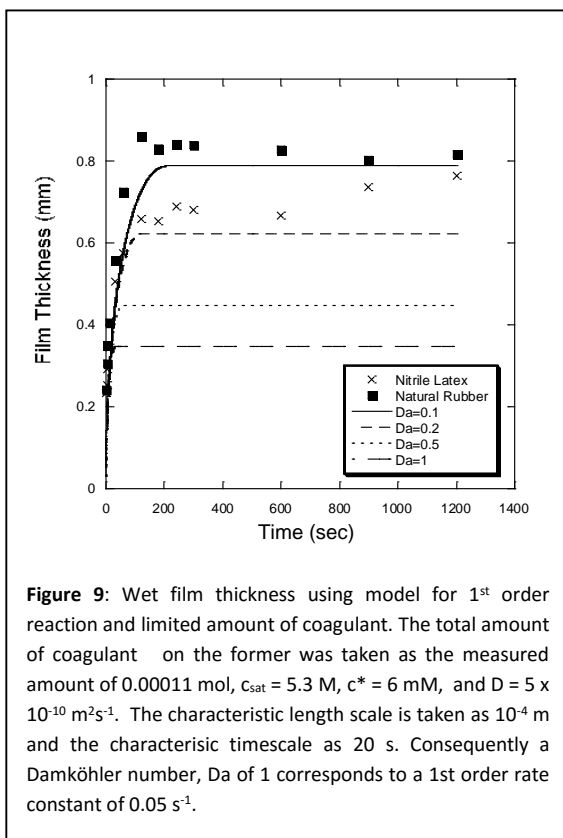


Figure 8: Effect of different solid contents and the corresponding rate constants for 1st order reaction. Parameters used were $c_{sat} = 5.3$ M, $c^* = 6$ mM, and $D = 5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$.



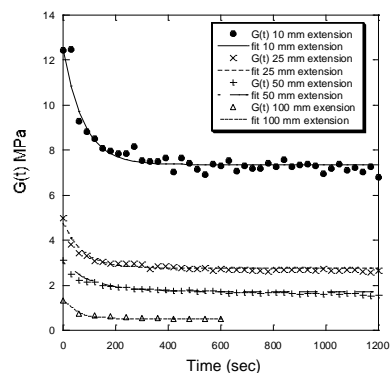


Figure 10: Stress relaxation modulus at various extensional strains for the nitrile latex film.

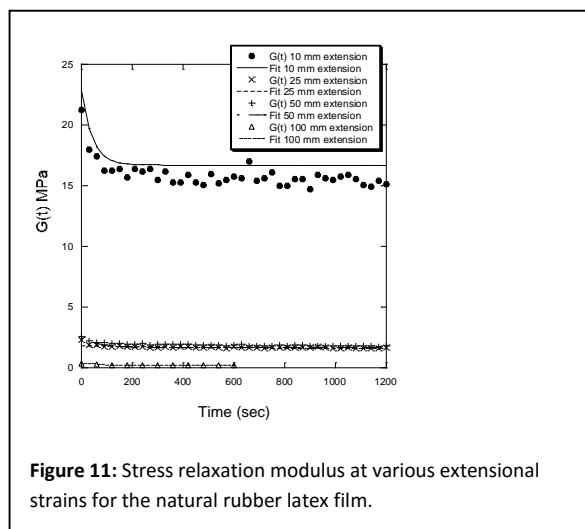


Figure 11: Stress relaxation modulus at various extensional strains for the natural rubber latex film.

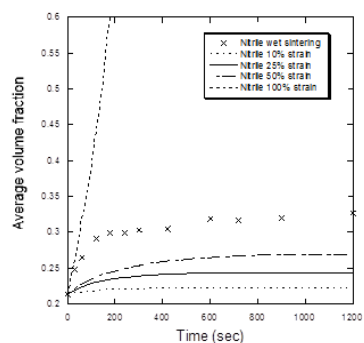


Figure 12: Wet sintering for nitrile latex using measured modulus data. For the numerical predictions the parameters were those listed in Tables 1 and 2. The dwell time was 5 seconds.

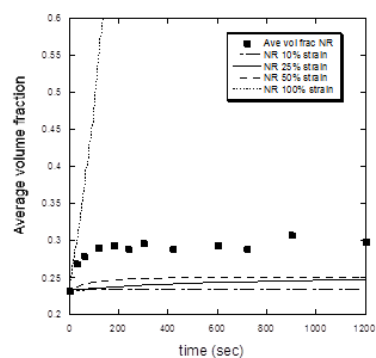


Figure 13: Wet sintering for natural rubber latex and wet sintering predictions. For the numerical predictions the parameters were those listed in Tables 1 and 2. The dwell time was 5 seconds.

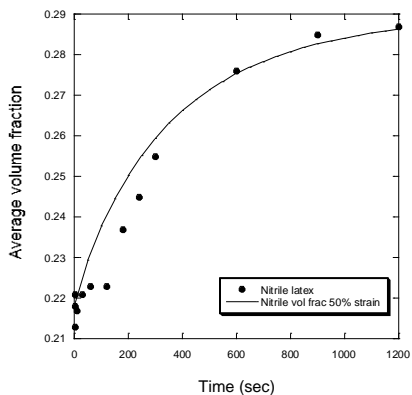


Figure 14: Predicted average volume fraction in nitrile latex film when it is put into latex bath and left for different times. For the numerical predictions the parameters were those listed in Table 1.

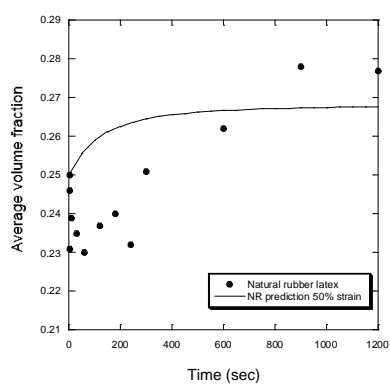


Figure 15: predicted average volume fraction in natural latex film when it is put into latex bath and left for different times. For the numerical predictions the parameters were those listed in Table 1.

*Table 1: Parameters used to provide
numerical predictions*

	Nitrile latex	Natural rubber latex
Critical coagulation concentration C^* (mM)	6	5.5
Polymer-water surface tension γ (mN/m)	12.9	12.9
Particle radius R_0 (nm)	80.5	227
Solubility limit for $\text{Ca}(\text{NO}_3)_2$ (M) ²³	5.3	
Diffusion coefficient for Ca^{2+} ions in water (m^2s^{-1}) ²⁴	5×10^{-10}	
Area of former (m^2)	0.002916	
Amount of coagulant on former (mol)	0.00011	

Table 2: Parameters used to fit measured stress relaxation data to the viscoelastic solid model.

	Ext (mm)	Strain %	G_1 (MPa)	G_2 (MPa)	η (MPa s)	τ (s)
Nitrile latex	10	10	7.36	5.12	396	77
	25	25	2.75	1.97	154	78
	50	50	1.72	1.28	147	115
	100	100	0.49	0.83	50	60
Natural rubber latex	10	10	16.7	6.14	258	42
	25	25	1.53	0.29	202	693
	50	50	1.65	0.81	55.5	68.5
	100	100	0.19	0.15	14.7	98

GRAPHICAL ABSTRACT

Robert Groves and Alexander F. Routh

INSIGHTS INTO FILM DEPOSITION AND CONSOLIDATION DURING THE THIN GLOVE COAGULANT DIPPING PROCESS

A model is presented that predicts the thickness of a latex film during glove dipping. The usual assumption of diffusional growth is shown to be accurate for early times but a subsequent departure is ascribed to reaction between the coagulant and surfactant

GRAPHICAL ABSTRACT FIGURE ((Please provide a square image to be produced at 50 mm wide by 50 mm high. Please avoid graphs and other figures with fine detail due to the relatively small size of this image.))

